7.6: Hess's Law

> **❰❱ Learning Objective**
>
> - Learn how to combine chemical equations and their enthalpy changes.

Now that we understand that chemical reactions occur with a simultaneous change in energy, we can apply the concept more broadly. To start, remember that some chemical reactions are rather difficult to perform. For example, consider the combustion of carbon to make carbon monoxide:

$$2\,C(s) + O_2(g) \rightarrow 2\,CO(g) \quad \Delta H = ?$$
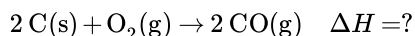
In reality, this is extremely difficult to do. Given the opportunity, carbon will react to make another compound, carbon dioxide:

$$2\,C(s) + O_2(g) \rightarrow 2\,CO_2(g) \quad \Delta H = -393.5 kJ$$
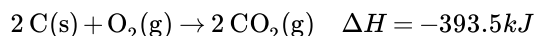
Is there a way around this? Yes. It comes from the understanding that chemical equations can be treated like algebraic equations, with the arrow acting like the equals sign. Like algebraic equations, chemical equations can be combined, and if the same substance appears on both sides of the arrow, it can be canceled out (much like a spectator ion in ionic equations). For example, consider these two reactions:

$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO_2(g)$$

$$2\,CO_2(g) \rightarrow 2\,CO(g) + O_2(g)$$
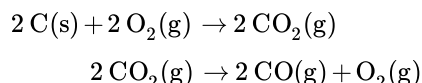
If we added these two equations by combining all the reactants together and all the products together, we would get

$$2\,C(s) + 2\,O_2(g) + 2\,CO_2(g) \rightarrow 2\,CO_2(g) + 2\,CO(g) + O_2(g)$$
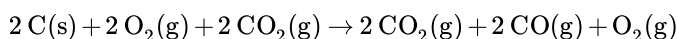
We note that $2\,CO_2(g)$ appears on both sides of the arrow, so they cancel:

$$2\,C(s) + 2\,O_2(g) + \cancel{2\,CO_2(g)} \rightarrow \cancel{2\,CO_2(g)} + 2\,CO(g) + O_2(g)$$
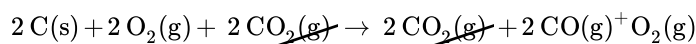
We also note that there are 2 mol of O$_2$ on the reactant side, and 1 mol of O$_2$ on the product side. We can cancel 1 mol of O$_2$ from both sides:

$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO(g) + O_2(g)$$
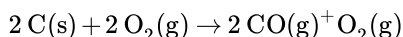
What do we have left?

$$2\,C(s) + O_2(g) \rightarrow 2\,CO(g)$$
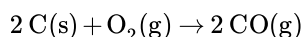
This is the reaction we are looking for! So by algebraically combining chemical equations, we can generate new chemical equations that may not be feasible to perform.

What about the enthalpy changes? **Hess's law** states that when chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way. Two corollaries immediately present themselves:

1. If a chemical reaction is reversed, the sign on ΔH is changed.
2. If a multiple of a chemical reaction is taken, the same multiple of the ΔH is taken as well.

What are the equations being combined? The first chemical equation is the combustion of C, which produces CO$_2$:
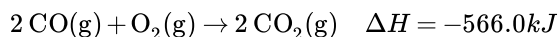
$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO_2(g)$$
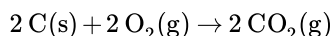
This reaction is two times the reaction to make CO_2 from $C(s)$ and $O_2(g)$, whose enthalpy change is known:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 kJ$$
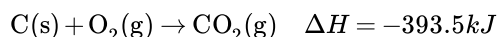
According to the first corollary, the first reaction has an energy change of two times −393.5 kJ, or −787.0 kJ:

$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO_2(g) \quad \Delta H = -787.0 kJ$$
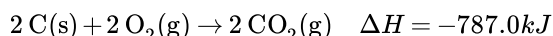
The second reaction in the combination is related to the combustion of CO(g):

$$2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g) \quad \Delta H = -566.0 kJ$$

The second reaction in our combination is the reverse of the combustion of CO. When we reverse the reaction, we change the sign on the ΔH:

$$2\,CO_2(g) \rightarrow 2\,CO(g) + O_2(g) \quad \Delta H = +566.0 kJ$$
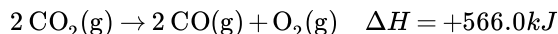
Now that we have identified the enthalpy changes of the two component chemical equations, we can combine the ΔH values and add them:

$$
\begin{cases}
2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -787.0 kJ \\
2CO_2(g) \rightarrow 2CO(g)) + O_2(g) \quad \Delta H = +566.0 kJ \\
------------------------- \\
2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta H = -787.0 + 566.0 = -221.0 kJ
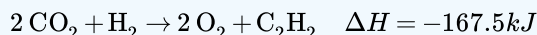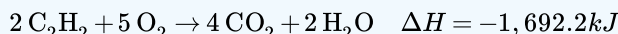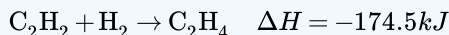\end{cases}
$$
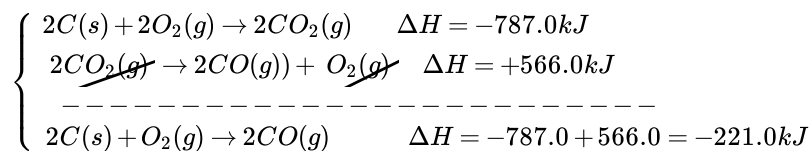
Hess's law is very powerful. It allows us to combine equations to generate new chemical reactions whose enthalpy changes can be calculated, rather than directly measured.

✔ **Example 7.6.1**

Determine the enthalpy change of

$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O \quad \Delta H = ?$$

from these reactions:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad \Delta H = -174.5 kJ$$

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \quad \Delta H = -1,692.2 kJ$$

$$2\,CO_2 + H_2 \rightarrow 2\,O_2 + C_2H_2 \quad \Delta H = -167.5 kJ$$
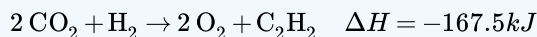
Solution

We will start by writing chemical reactions that put the correct number of moles of the correct substance on the proper side. For example, our desired reaction has C_2H_4 as a reactant, and only one reaction from our data has C_2H_4. However, it has C_2H_4 as a product. To make it a reactant, we need to reverse the reaction, changing the sign on the ΔH:

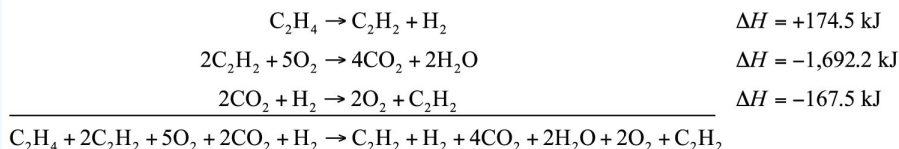$$C_2H_4 \rightarrow C_2H_2 + H_2 \quad \Delta H = +174.5 kJ$$
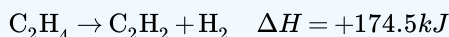
We need CO_2 and H_2O as products. The second reaction has them on the proper side, so let us include one of these reactions (with the hope that the coefficients will work out when all of our reactions are added):
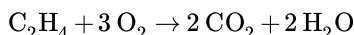
$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \quad \Delta H = -1,692.2 kJ$$
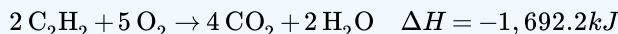
We note that we now have 4 mol of CO_2 as products; we need to get rid of 2 mol of CO_2. The last reaction has $2CO_2$ as a reactant. Let us use it as written:

$$2\,CO_2 + H_2 \rightarrow 2\,O_2 + C_2H_2 \quad \Delta H = -167.5 kJ$$

We combine these three reactions, modified as stated:

$C_2H_4 \rightarrow C_2H_2 + H_2$	$\Delta H = +174.5$ kJ
$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$	$\Delta H = -1,692.2$ kJ
$2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2$	$\Delta H = -167.5$ kJ
$C_2H_4 + 2C_2H_2 + 5O_2 + 2CO_2 + H_2 \rightarrow C_2H_2 + H_2 + 4CO_2 + 2H_2O + 2O_2 + C_2H_2$	

What cancels? $2C_2H_2$, H_2, $2O_2$, and $2CO_2$. What is left is

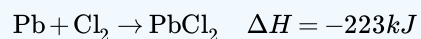$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$

which is the reaction we are looking for. The ΔH of this reaction is the sum of the three ΔH values:

$$\Delta H = +174.5 - 1{,}692.2 - 167.5 = -1{,}685.2 \text{ kJ}$$

> **?** **Exercise 7.6.1**
>
> Given the thermochemical equations
>
> $$\text{Pb} + \text{Cl}_2 \rightarrow \text{PbCl}_2 \quad \Delta H = -223 kJ$$
>
> $$\text{PbCl}_2 + \text{Cl}_2 \rightarrow \text{PbCl}_4 \quad \Delta H = -87 kJ$$
>
> determine ΔH for
>
> $$2\,\text{PbCl}_2 \rightarrow \text{Pb} + \text{PbCl}_4$$
>
> **Answer**
>
> +136 kJ
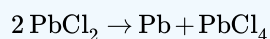
Key Takeaway

- Hess's law allows us to combine reactions algebraically and then combine their enthalpy changes the same way.